Reversible crosslinking: a potent paradigm for designer materials

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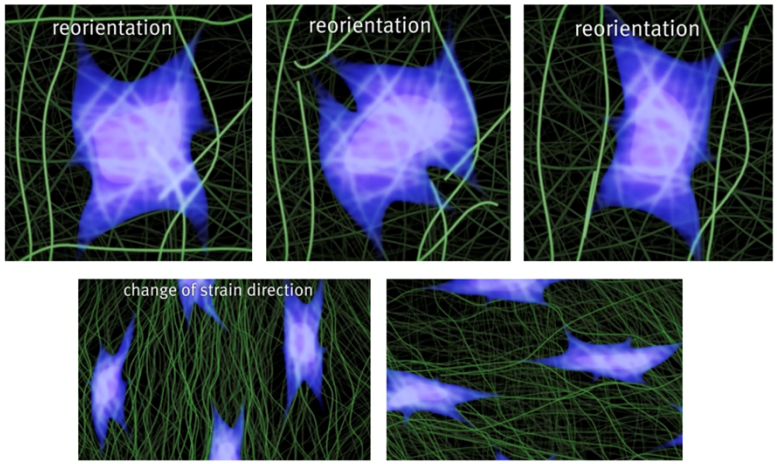
Motivation

Soft materials are dynamic;
the molecules comprising them are always in motion.

Collagen

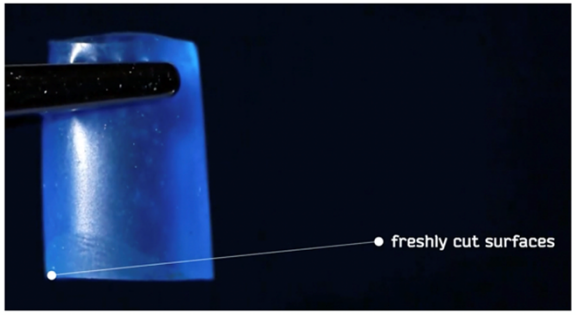


https://www.youtube.com/watch?v=atalSlZSuf8

Vitrimers

http://www.univ-psl.fr/default/EN/all/psl_en/the_vitrimer.htm

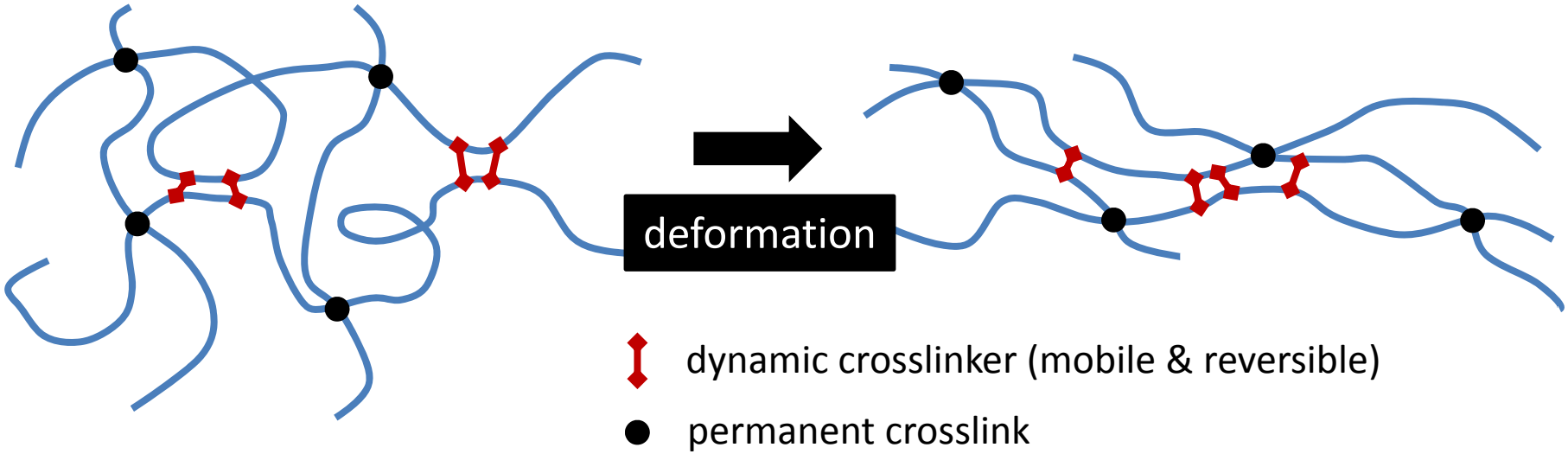
Self-Healing Materials



Cordier et al., Nature 451, 977–980 (2008)
Suprapolix

Dynamic Bonds in Materials

Reversible crosslinks break and re-form, depending on how the system is perturbed.



Recent Examples

biopolymer networks — C.P. Broedersz *et al.*, *Phys. Rev. Lett.* **105** 23101 (2010).

vitrimers — M. Capelot *et al.*, *ACS Macro Lett.* **1** 789 (2012)

reversibly-crosslinked materials — C.J. Kloxin and C.N. Bowman, *Chem. Soc. Rev.* **42** 7161 (2013).

Z.S. Kean *et al., Adv. Mater.* **26** 6013 (2014).

hydrogels assembled *in-situ* — E.R. Draper *et al.*, *Nat. Chem.* **7** 848 (2015).

self-healing and recyclable rubber — L. Imbernon *et al.*, *Macromolecules* **49** 2172 (2016).

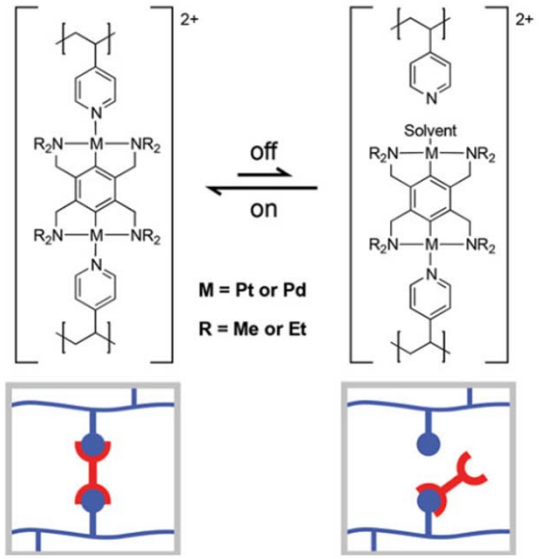
Example

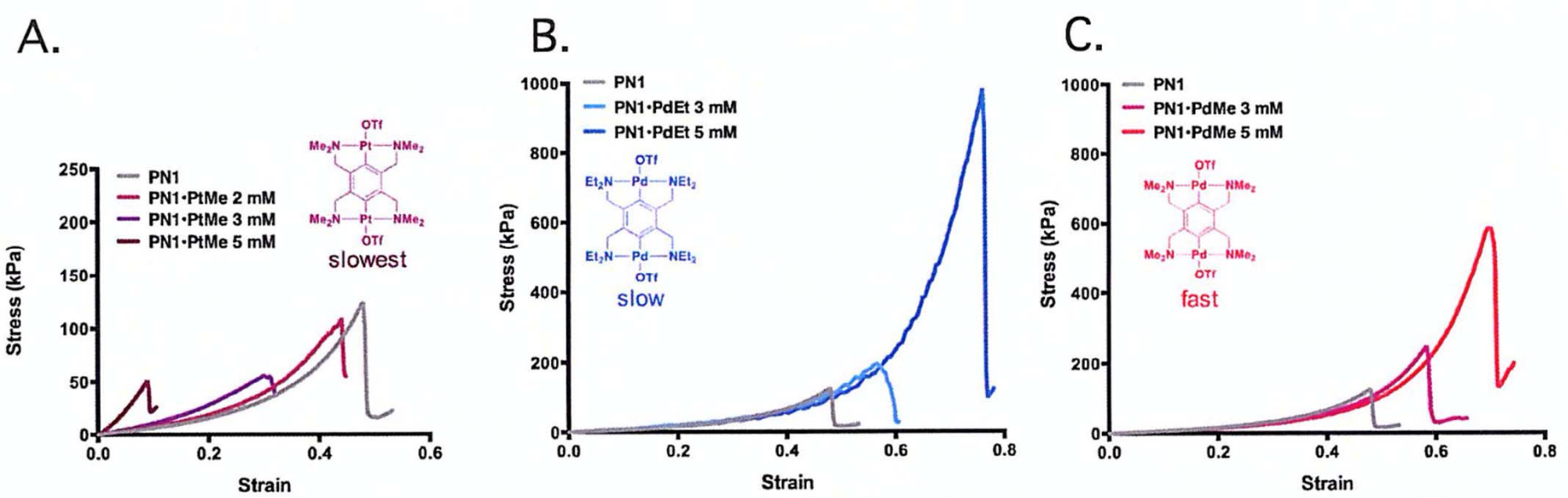
Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

Increasing the Maximum Achievable Strain of a Covalent Polymer Gel Through the Addition of Mechanically Invisible Cross-Links

*Zachary S. Kean, Jennifer L. Hawk, Shaoting Lin, Xuanhe Zhao, Rint P. Sijbesma, and Stephen L. Craig**





Probing with Theory & Simulation

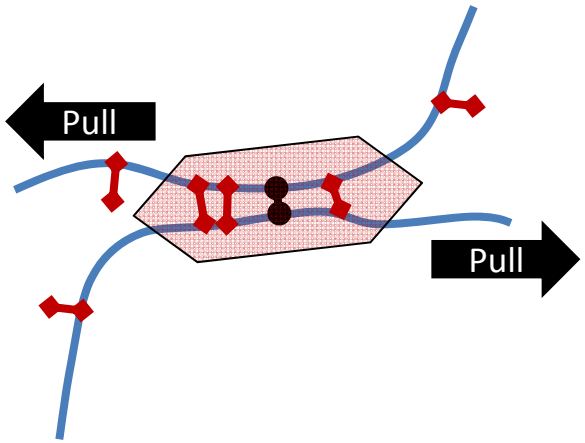
Theory and simulation are a valuable tool for understanding microscopic behaviour, and making macroscopic predictions.

Some of the key questions we seek to explore:

- Where in the system does reversible bonding happen? Are they recruited around permanent crosslinks?
- How do reversible bonds improve the strength of connectivity between individual polymers?
- How do the reversible bonds respond to deformation of the system? How does this depend on deformation rate?
- Are there “design principles” for optimising a system with reversible bonding, depending on the desired application?

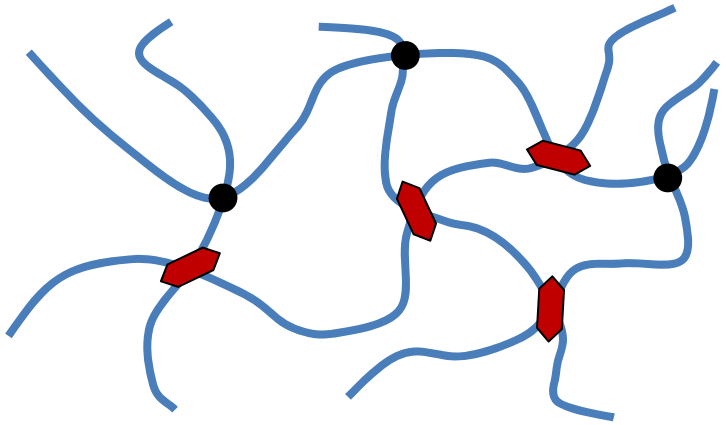
Two Scales of Modeling

Molecular scale



reversible crosslink
permanent crosslink

nano- & meso-scale



"coarse-grained" reversible crosslinking region
permanent crosslink

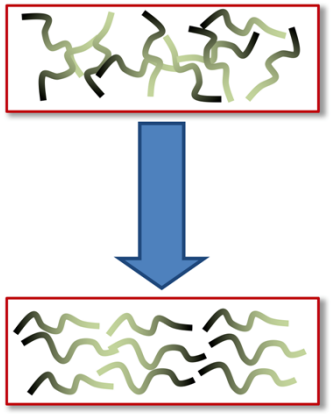
Structure and dynamics at the molecular scale:

- reversible crosslink lifetimes, chemical composition, chain architecture
- spatial correlations & dynamics near permanent crosslinks
- local response to perturbations, dependence on spatial structure

Mechanical response at the macroscopic scale:

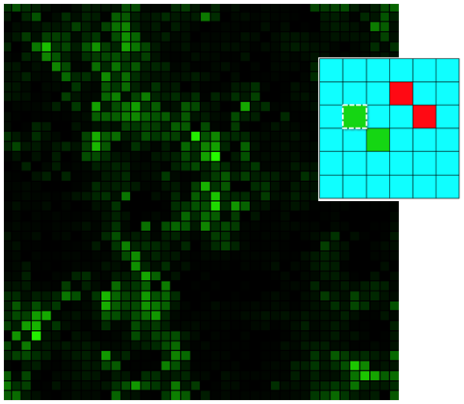
- dependence on crosslink lifetimes
- effect of crosslink density, ratio of permanent to reversible links
- dependence on deformation rate

My Background



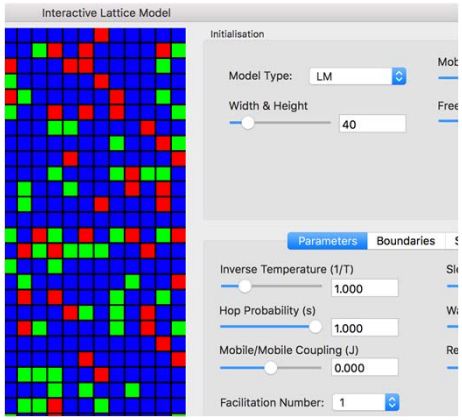
Copolymer phase behaviour

Macromolecules 10.1021/ma102296r
Macromolecules 10.1021/ma3011558

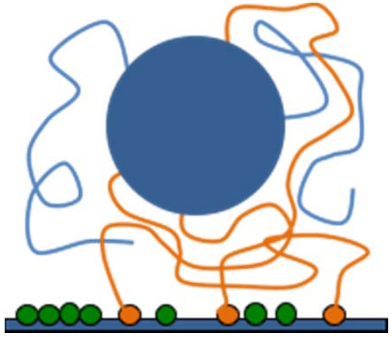


Liquid / polymeric glasses

Soft Matter 10.1039/c3sm25679k
Soft Matter 10.1039/c3sm51287h
Soft Matter 10.1039/c5sm01701g
Rep. Prog. Phys., submitted

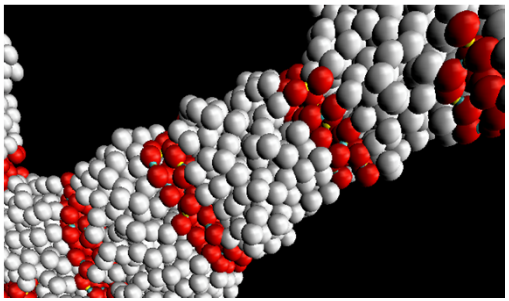


End-user app development



Superselective multivalent particles / polymers

Macromolecules 10.1021/ma5014918
JCP Comm. 10.1063/1.4948257
EPJST 10.1140/epjst/e2016-60119-6

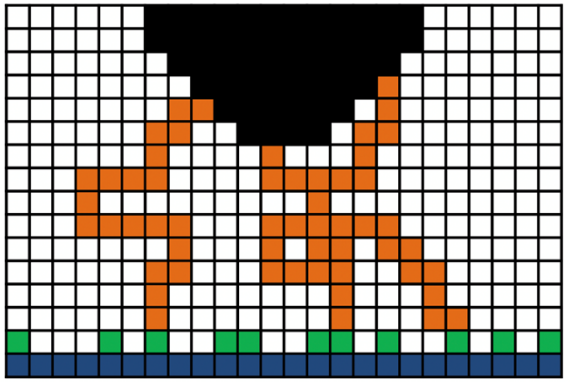


Self-assembling supramolecular polymers

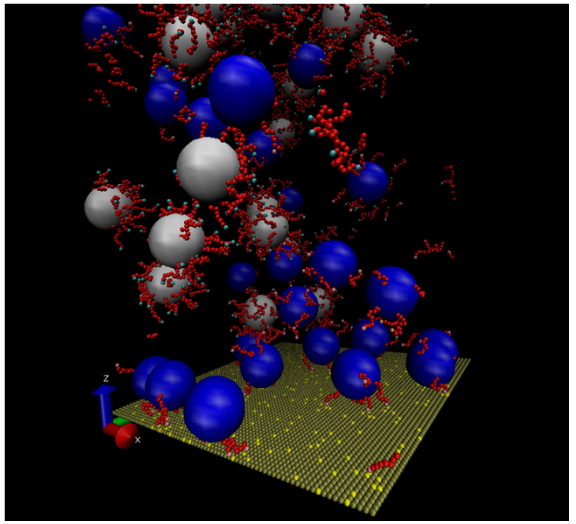
Photo-actuated liquid crystal films

Research Approach

Numerical methods & simplified models
lattice models(self-consistent) mean field theory



Molecular simulation
GPU molecular dynamics, Monte Carlo



Theory
multivalent interactions, free energy calculations

$$\Delta F \propto N_R \left(\ln q_b - \ln q_{ub} \right)$$

Hopeful Collaborations

Physical Chemistry & Soft Matter

van der Gucht. *Self-assembled polymer networks*
Leermakers. *Self-consistent field theory & applications*
Kamperman. *Bio-inspired functional polymers*

Chemical Engineering, Advanced Soft Matter

Eelkema & van Esch. *Self-assembling materials and out-of-equilibrium assembly*
Tighe. *Modeling deformation and flow in soft solids and complex fluids*

Department of Chemistry

Broer & Liu. *Stimulus-responsive polymeric materials*
Sijbesma. *Bio-inspired polymers and networks*

Biomaterials Science & Technology

Materials Science & Technology of Polymers

Hopeful Collaborations

“International Expert”

Costantino Creton. *Multi-component and pre-strained polymer networks, vitrimers*

External Collaborations (existing and potential):

Imperial College London

Stefano Angioletti-Uberti
multivalent design

Eric Appel
polymer networks with reversible supramolecular crosslinks

Bortolo Mognetti
supramolecular kinetics, multivalency

Dave Adams
self-assembled in-situ hydrogels